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# Seasonal variation of particulate lipophilic organic compounds at nonurban sites in Europe

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[1] Atmospheric aerosol samples, collected continuously during a sampling period longer than 1 year at six rural and background sites representing oceanic, rural and continental environments across Europe, were extracted, fractionated and analyzed by gas chromatography/mass spectrometry. The detailed organic speciation of the aerosol samples enabled the choice of some key compounds to assess the contribution of different sources. Lipophilic molecular markers were identified, including vehicle exhaust constituents, meat smoke tracers, phytosterols of higher photosynthetic plants and wood smoke components, especially from coniferous vegetation. The lowest concentrations and a quasi absence of seasonal cycle were observed at the oceanic background site of Azores. The highest values and a greater number of compounds were registered at the two continental lower-level sites. Aveiro (a rural site close to the small coastal Portuguese city of Aveiro) and K-puszta (Hungarian plains) both presented a seasonal variation with winter maxima attributable to a sizable contribution of wood-burning and meat-cooking sources. At the mountain sites (Puy de Dôme, Schauinsland and the high alpine summit of Sonnblick), concentrations maximized during summer as a result of the decoupling of the lower layers from the midtroposphere with wintry weather and the influence of boundary layer air masses during the warm season.

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## 1. Introduction

[2] Aerosol particles are ubiquitous components of the atmosphere and include inorganic substances such as sulfates and carbonaceous species, which are divided into organic carbon (OC) and elemental carbon (EC). The increasing consciousness of the impact of atmospheric particles on climate, and the incompletely recognized but serious effects of anthropogenic aerosols on air quality and human health, motivated numerous scientific studies. Those studies have shown that particulate phase organic compounds could account for 20–50% of the atmospheric aerosol mass [*Guo et al.*, 2003; *Pio et al.*, 2001a]. Determining the sources of carbon-containing aerosols has been hampered by the complex nature of these materials and by a poor knowledge of the transformation processes that take place in the particle phase. The great number of samples necessary to trace contributions from specific emission sources makes such an investigation costly and time consuming. Thus most studies to date, aiming at a detailed characterization of organic aerosols, rely on the implementation of brief field experiments. Even studies of seasonal evaluation are usually based on two independent short-term sampling campaigns, performed during both summer and winter representative periods.

[3] Some studies have focused on the assessment of natural versus anthropogenic contributions to the carbonaceous aerosol by searching molecular markers or tracers, which include organic compounds that are source specific, react slowly in the atmosphere, and do not partition to the gas phase during the transport [e.g., *Schauer et al.*, 1996; *Schauer and Cass*, 2000; *Simoneit*, 1989, 1999, 2002; *Zheng et al.*, 2002; *Simoneit et al.*, 2004; *Leithead et al.*, 2006; *Li et al.*, 2006; *Subramanian et al.*, 2006; *Wang et al.*, 2007]. These studies indicate that biomass and fossil fuel combustion supply high loads of molecular markers to organic aerosols. However, in spite of the considerable work that has been done in the organic characterization of specific source emissions (motor vehicle exhaust, food-cooking operations, fireplace combustion of wood, etc.), studies focused on the differences in the molecular compo-

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**Table 1.** Characterization of the Sampling Sites

| Site | Abbreviation | Altitude Above Sea Level, m | Coordinates | Main Characteristics | Type of Particulate Matter Sampled |
|---|---|---|---|---|---|
| Azores, Terceira island, Portugal | AZO | 50 | 38°41′N, 27°21′W | background marine atmosphere | $PM_{2.5}$ |
| Aveiro, Moitinhos, Portugal | AVE | 40 | 40°35′N, 08°38′W | Atlantic coast, rural | $PM_{2.5}$ |
| Puy de Dôme, France | PDD | 1450 | 45°46′N, 02°57′E | rural highlands | $PM_{10}$ |
| Schauinsland, Germany | SIL | 1205 | 47°55′N, 07° 54′E | forested highlands | $PM_{10}$ |
| Sonnblick, Austria | SBO | 3106 | 47°03′N, 12°57′E | mountain peak in the central Alps | $PM_{2.5}$ |
| K-Puszta, Hungary | KPZ | 136 | 46°58′N; 19°35′E | large Hungarian plains surrounded by forests | $PM_{2.0}$ |

sition to infer the diverse contributions to the ambient aerosol were essentially conducted in regions impacted by biomass burning or in metropolitan areas very influenced by traffic. Long-term studies of lipophilic organic markers in atmospheric aerosols of more pristine environments are still scarce. Moreover, the relative contribution of natural versus anthropogenic sources is not fully known and hence the extent to which the fragile natural equilibrium of the atmosphere has been disturbed is scantily understood. The establishment of a comprehensive aerosol data set, lacking till now, for various environmental conditions in Europe (marine/continental, rural/urban, boundary layer/free troposphere, and winter/summer) will contribute to (1) improve emission inventories, (2) develop climate models, (3) establish source/receptor relationships that govern the individual compounds present in the breathable complex organic mixtures and, (4) consider environmental policies foreseeing possible emission control strategies.

[4] This work presents a year-round study of lipophilic particulate organic compounds at different nonurban sites located along a west-east transect in Europe, from the Azores to Hungary, crossing highly elevated Alpine sites. It should be stressed that measurements were taken without interruption and under very hard conditions in certain locations, such as a cliff in a remote island in the middle of the North Atlantic Ocean, or the top of a permanently frozen Alpine mountain. The seasonal variation of particle-associated homologous compound sequences, specific lipophilic organic tracers and diagnostic parameters were analyzed to establish a chemical fingerprint of emission sources contributing to atmospheric aerosols on a continental scale. This investigation represents, as far as we know, the most extensive temporal and spatial study of the detailed constitution of atmospheric lipophilic organic aerosols across seasons of nonurban Europe, the free troposphere, or the central Atlantic region.

## 2. Experimental Section

[5] Integrated in the EU Project CARBOSOL, high-volume samplers were used, from July 2002 to September 2003, to collect atmospheric particulate matter on preheated quartz fiber filters. The sampling sites are listed in Table 1. These sites provide a west-east transect across Europe going from the middle of the Atlantic Ocean to the plains of eastern Europe. The detailed characterization of the sampling sites and a map showing their locations could be found in a companion paper [*Pio et al.*, 2007]. At four sites very similar size cuts of 2–2.5 $\mu$m were used and the aerosol fraction collected was quite similar. At the other two locations, the available equipment capable of resolving problems of sampling in subfreezing conditions implied that $PM_{10}$ samples had to be collected. Collection of $PM_{10}$, instead of $PM_{2.5}$, in the two mountain sampling sites of SIL and PDD may influence the values obtained for compounds present predominantly in coarse particles originated from sources such as dust from soil origin, although at these high altitudes this is presumed to be a far less serious interference than it would be at lowland dustier environments. A size distribution study carried out with different types of air masses at PDD have showed that, except during a sporadic Saharan dust event, the organic aerosol mass is chiefly present below 3 $\mu$m [*Sellegri et al.*, 2003]. To collect an adequate amount of material for performing all CARBOSOL analysis, even at remote oceanic and mountain sites, weekly sampling was carried out in order to guarantee masses of the target compounds higher than the detection limits of the analytical procedures. Because of the extended sampling period, volatilization/condensation processes for semivolatile organics may have occurred. Also, oxidation of filter-deposited organics by strong oxidants, such as ozone, may have happened during sampling. Measured concentrations for oxygenated organic species represent therefore an upper limit of the true atmospheric levels [*Pio et al.*, 2001b]. It can, however, been assumed that, during sampling, equilibrium between gas and particulate phase would govern the behavior of the filtered aerosol similarly to what occurs in the atmosphere. In addition, the large mass of particles collected would reduce potential adsorption of semivolatile organic compounds on active sites of the quartz fiber surfaces, as result of their rapid saturation.

[6] The weekly aerosol filters collected at the six sites were analyzed by a thermal-optical technique to determine the EC and OC content [*Castro et al.*, 1999; *Pio et al.*, 1994]. On the basis of their organic carbon content, filters from weekly samples were pooled on a monthly basis and were extracted for 24 hour periods, first with dichloromethane (DCM) (Merck Suprasolv), and then with methanol (Merck Suprasolv). After drying, the mass of the combined extract residues was determined by weighing. Methanol extracts were stored in the freezer and are still awaiting analysis. The total organic extracts obtained by DCM, were fractionated by flash chromatography [*Alves et al.*, 2001; *Gogou et al.*, 1998; *Stephanou and Stratigakis*, 1993]. This technique includes the use of eluents of increasing polarity (Merck Suprasolv) and elution through activated silica-gel (230–400 mesh, 60 Å Merck Grade 9385) under nitrogen flow, resulting into five different fractions of increasing polarity: (1) 15 mL *n*-hexane (fraction 1, aliphatics); (2) 15 mL toluene-*n*-hexane (5.6:9.4) [fraction 2, polycyclic aromatic hydrocarbons (PAH)]; (3) 15 mL *n*-hexane-DCM

**Table 2.** Seasonal Average Concentrations of Organic Carbon, Elemental Carbon and Ratio Between the DCM Extract and the Estimated Organic Matter for the Six CARBOSOL Sites[a]

| | AZO | AVE | PDD | SIL | SBO | KPZ |
|---|---|---|---|---|---|---|
| OC, $\mu$g m$^{-3}$ | 0.53 (S), 0.38 (W) | 4.30 (S), 10.43 (W) | 3.35 (S), 1.11 (W) | 4.75 (S), 1.92 (W) | 1.94 (S), 0.67 (W) | 6.80 (S), 10.32 (W) |
| EC, $\mu$g m$^{-3}$ | 0.07 (S), 0.06 (W) | 0.91 (S), 1.88 (W) | 0.36 (S), 0.25 (W) | 0.49 (S), 0.31 (W) | 0.32 (S), 0.77 (W) | 0.97 (S), 2.20 (W) |
| DCM extract,[b] % | 46.6 | 66.6 | 30.3 | 49.7 | 68.6 | 61.3 |

[a] S, summer; W, winter.

[b] Average ratio between the DCM extract mass and the OM mass.

(7.5:7.5) (fraction 3, carbonyl compounds and oxy-PAH); (4) 20 mL ethyl acetate-*n*-hexane (8:12) (fraction 4, *n*-alkanols, sterols and other hydroxyl compounds); and (5) 20 mL solution of pure formic acid in methanol (4%, v/v) (fraction 5, acids). After each elution, the different fractions were vacuum concentrated (25–30°C under reduced pressure) and evaporated by a gentle ultrapure nitrogen stream. This methodology was previously tested in our laboratory [*Alves*, 2001; *Carvalho*, 2003] and elsewhere [*Gogou et al.*, 1998].

[7] The fractionated extracts were analyzed by gas chromatography/mass spectrometry (GC/MS). The operation conditions were as follows (GC-HP 6890 and MS-HP 7873, quadrupole): (1) capillary column, RTx–5MS; 25 m; 0.25 mm internal diameter; 0.25 $\mu$m film thickness; (2) flow and type of carrier gas, Helium, 1.0 mL min$^{-1}$; (3) acquisition mode, electron ionization at 70 eV; (4) interface and ion source temperature, 250°C, 230°C; (5) scanned masses, 33 to 800 m/z; (6) injection mode, splitless; and (7) heating program, 60°C, 1 min; 60°C to 80°C, 10°C min$^{-1}$; 80°C to 290°C, 7°C min$^{-1}$; 290 °C, 20 min. To monitor the instrument sensitivity, for each GC/MS run, *p*-terphenyl (Aldrich T320-3) and tetracosane-D$_{50}$ (Aldrich 45.177-0) were used as internal standards. Fractions 4 and 5 include more polar compounds, which require derivatization for analysis with GC/MS. To fraction 4, between 25 and 100 $\mu$L of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA): Trimethylchlorosilane (TMCS) 99:1 (Supelco 33149-U) were added, to convert alcohols into the corresponding TMS ether derivatives (samples were placed in an oven at 70°C for 3 hours). To fraction 5, freshly prepared diazomethane (using Diazald 99% Aldrich D2.800-0) was added in order to convert organic acids into the methyl ester derivatives [*Blau and Halket*, 1993]. Compound identification was based on the GC/MS spectra library and on coinjection with 70 authentic standards. Compounds within the homologous series for which standards were not available were identified by comparing their spectra to the standards for similar compounds within the series, by comparison to the Wiley mass spectral library, and by the analysis of fragmentation patterns. Relative response factors were calculated for 3–10 standard compounds, representing each compound class, of increasing molecular mass. Relative response factors for specific constituents (e.g., some molecular tracers) were calculated for each single compound individually. Recovery tests were carried out by spiking quartz fiber filters with a standard mixture of compounds, about 10 ng each, which corresponds to an air concentration of 4 pg m$^{-3}$. All the extraction, derivatization and quantification procedure was repeated. The amount of each recovered standard was determined with an internal standard. The results were calculated from the previously determined relative response factors. The mean recoveries ranged from 60 to 99%, depending on the analyte. The lower value was obtained for phenanthrene. The recoveries of individual compounds within the main homologous series of *n*-alkanes, *n*-alkanols and *n*-alkanoic acids were higher than 95%. The GC/MS precision based on repetitive analysis for every twelfth sample ranged from 1.5% for *n*-octacosane to 7.1% for *n*-tetradecanal, and less than 5.0% for most compounds. Field blanks were prepared, stored and handled by exactly the same procedures as used for the ambient samples. The total blank weight never exceeded 2% of the individual sample extracts, except for the acid fraction, where the maximum contamination represented 8% of the total fraction extract. The most frequent contaminants were phthalate esters, which did not interfere with the quantification of compounds of interest. All quantities here provided were corrected, taking into consideration the application of the analytical methodology with standard compounds (column chromatography performance and relative response factors in GC/MS). Limits of detection for individual compounds (typically 0.02–0.08 pg m$^{-3}$, depending on the analyte) were defined as the mean blank mass plus three standard deviations.

## 3. Results and Discussion

### 3.1. Carbonaceous Content and Organic Matter Extracts

[8] Throughout this paper, "summer" will represent the 6-month period from April to September, and "winter" the complementary time interval. Table 2 presents average seasonal concentrations of OC and EC at the six sampling sites. The levels of carbonaceous aerosol are high at the continental lowland sites of KPZ and AVE and small at the mountainous locations of SIL, PDD, SBO, being minimal at the remote oceanic site of AZO. At AVE and KPZ, carbonaceous aerosol levels peak clearly in winter. Oppositely, in the mountain sites maximum levels are reached during summer, with seasonal patterns differently affected by emissions and vertical transport. The concentrations measured are similar to those presented in other studies for continental (K-Puszta, Hungary: OC = 7.1 $\mu$g m$^{-3}$; EC = 0.42 $\mu$g m$^{-3}$ [*Molnár et al.*, 1999]), marine (San Nicolas Island, USA: OC = 1.5 $\mu$g m$^{-3}$; EC = 0.16 $\mu$g m$^{-3}$ [*Chow et al.*, 1994]), and rural and coastal areas (Tábua, Anadia, and Areão, Portugal: OC = 1.0 $\mu$g m$^{-3}$ to 6.8 $\mu$g m$^{-3}$; EC = 0.3 $\mu$g m$^{-3}$ to 1.7 $\mu$g m$^{-3}$ [*Castro et al.*, 1999]). A more detailed analysis of the nature of the particulate organic matter based on the separation of OC into four fractions of increasing volatility and the estimation of OC that has a secondary origin can be found in a companion paper by *Pio et al.* [2007].

[9] The DCM extractable material was found to account for average values between 30% in PDD and 69% in SBO of the organic matter (OM), which was calculated from the concentration of OC by multiplying by an organic mass to carbon mass ratio of 1.6 [*Turpin et al.*, 2000]. It should be noted that a significant portion of the more polar oxygenated organic compounds are not extractable by DCM. The bulk of organic carbon representing more hydrophilic compounds (e.g., dicarboxylic acids, sugar polyols, anhydrosugars, cellulose and humic-like substances) was determined using methodologies developed by other CARBOSOL teams, whose results can be found in companion papers.

[10] The mass of chromatographically elutable organics can be subdivided into resolved (identifiable peaks) and unresolved complex mixture (UCM), consisting above all of cyclic and branched chain hydrocarbons from the incomplete combustion of fossil fuels [*Tang et al.*, 2006]. About 200 individual organic compounds present in the aerosol phase were identified and quantified by GC/MS. The organic matter that is chromatographically identifiable ranged from 2% (PDD and SIL) to 4% (AZO and KPZ). Similar percentages were obtained in other rural areas [*Brown et al.*, 2002; *Gogou et al.*, 1996; *Pio et al.*, 2001b]. The extractable organic fractions that could be separated chromatographically into identifiable compounds are limited to molecules with carbon atoms, in general, less than 40. Thus macromolecular and other complex components, resulting from oligomerization and polimerization processes, which are expected to exist in aged aerosol particles as result of either direct emission or from secondary transformation processes, constitute a fraction that could not be analyzed using the methodology followed in the present work. The chromatographically identifiable organic material consisted mainly of fatty acids, fatty alcohols and *n*-alkanes, with minor amounts of aldehydes, aromatic compounds and ketones, for all the sampling sites (Table 3 and Figure 1). The lowest average concentrations of the total chromatographically identifiable organic compounds were observed at the Atlantic Portuguese archipelago of Azores, where interseason variations were not appreciable. The sources for the organic aerosol at the Azores are possibly long-range transport, oceanic impaction and some local emissions, contributing to atmospheric levels characteristic of remote sites. In agreement with the seasonal patterns of OC, the highest values were registered at the two continental low-level sites, which presented a seasonal variation with winter maxima of 282 ng $m^{-3}$ and 446 ng $m^{-3}$, respectively for AVE and KPZ. At the higher mountain sites a summer maximum for the total concentrations of organics was observed. These elevated locations are influenced by boundary layer air masses during summer, while during the cold season air masses are decoupled from the air below the mixing layer as an effect of stable conditions with regular cloud layers well below the sampling stations. Thus, in winter, free tropospheric conditions are attained, whereas thermal mixing and cloud venting seam to lift up the mixed layers to those elevated sites in the warm season [*Kasper and Puxbaum*, 1998]. The results obtained for AVE and KPZ are in the lower end of the typical concentration range for total lipids in continental areas (100–10,000 ng $m^{-3}$). The values obtained in all other locations (AZO, PDD, SIL, and SBO) are within the characteristic range for more remote/oceanic regions (0.1–100 ng $m^{-3}$) [*Simoneit*, 1986].

## 3.2. Speciation of Particulate Organic Compounds

[11] The identification and quantification of homologous compound sequences (*n*-alkanes, *n*-alkanols, and *n*-alkanoic acids) present in chromatographically elutable fractions, in conjunction with the application of diagnostic parameters, provide helpful data relevant to the characterization of emission sources. The carbon preference index (CPI) has been proposed as an empirical utensil to evaluate qualitatively the weight of biogenic and anthropogenic inputs. For *n*-alkanes, this parameter is a ratio of the sum of odd-numbered hydrocarbons to the sum of even-numbered hydrocarbons. For *n*-alkanols and *n*-alkanoic acids, CPI is determined by inverting the ratio in order to have even-to-odd homologues. In general, the homologue compounds from epicuticular waxes of terrestrial plants exhibit high CPI values ($CPI \gg 1$). CPI values near unity indicate the presence of carbon homologues derived from petroleum products or from partial thermal alteration (i.e., incomplete combustion products) of petroleum [*Abas and Simoneit*, 1996; *Simoneit*, 1989, 1999; *Pio et al.*, 2001a, 2001b]. $C_{max}$, the carbon number with maximum concentration in the homologous series, can also be used as an indication of relative source inputs, especially to assess the contribution of waxy components of vegetation at a regional level [*Simoneit*, 1989]. The concentrations of wax *n*-alkanes, *n*-alkanols and *n*-alkanoic acids (WNA, WNAL and WNAC) are calculated by subtraction of the average of the next higher and lower even carbon numbered homologues, taking as zero the negative values [*Simoneit*, 1999]. Another diagnostic parameter that can be used to assess the magnitude of petroleum contributions to atmospheric aerosols is U:R (unresolved to resolved mass ratio) [*Tang et al.*, 2006].

### 3.2.1. Aliphatic Hydrocarbons

[12] The *n*-alkanes varied from $C_{13}$ to $C_{34}$ homologues (Table 3), with an odd carbon number predominance, and maximizing for the homologues $\geq C_{23}$, which are attributable to plant waxes [*Abas and Simoneit*, 1996]. The average concentration of the total homologous series ranged between 1.0 ng $m^{-3}$ (AZO) and 40.3 ng $m^{-3}$ (KPZ), presenting higher levels in winter, as opposed to the other sites. The homologues with less than 20 carbon atoms presented, throughout the campaign, low average concentrations (<1.1 ng $m^{-3}$). *Simoneit and Mazurek* [1982] explain this finding by sampling and extraction deficiencies resulting from the high volatility of these compounds. Therefore concentrations for *n*-alkanes < $C_{20}$ must be interpreted with caution. The dominance of the *n*-$C_{27}$, *n*-$C_{29}$ and *n*-$C_{31}$ homologues during summer shifted toward lower carbon numbers in the range *n*-$C_{21}$-*n*-$C_{25}$ during the colder season. Changes in the modal chain length of *n*-alkane distributions have been attributed to differences in growing season temperatures of the source regions [*Simoneit et al.*, 1991]. However, *Schefuß et al.* [2003] suggest a large influence of the regional precipitation regime on the chain length distributions of leaf wax lipids, in agreement with their biologic functionality as regulators of the plant moisture balance. It is also probable that the *n*-$C_{21}$-*n*-$C_{25}$ modal chain length in winter has resulted

**Table 3.** Summary of Analytical Results for Organic Aerosol of CARBOSOL Sites[a]

| | AZO | AVE | PDD | SIL | SBO | KPZ |
|---|---|---|---|---|---|---|
| Total average concentration of identified compounds, ng $m^{-3}$ | 19.2 (S), 17.8 (W) | 114.8 (S), 282.3 (W) | 64.4 (S), 16.9 (W) | 78.0 (S), 21.1 (W) | 47.7 (S), 28.0 (W) | 221.2 (S), 446.0 (W) |
| *n*-alkanes | | | | | | |
| Average concentration, ng $m^{-3}$ | 1.3(S), 0.7(W) | 14.3(S), 20.0(W) | 9.7(S), 2.8(W) | 10.8(S), 3.6(W) | 4.2(S), 3.8(W) | 37.3(S), 43.3(W) |
| Maximum concentration, ng $m^{-3}$ | 1.6 ($C_{31}$) | 10.3 ($C_{22}$) | 6.6 ($C_{29}$) | 8.4 ($C_{27}$) | 1.3 ($C_{31}$) | 21.5 ($C_{27}$) |
| Carbon range | $C_{13}-C_{33}$ | $C_{13}-C_{33}$ | $C_{13}-C_{33}$ | $C_{13}-C_{34}$ | $C_{13}-C_{33}$ | $C_{13}-C_{33}$ |
| $C_{max}$ | $C_{27}$; $C_{29}$; $C_{31}$ | $C_{22}$; $C_{27}$; $C_{29}$; $C_{31}$ | $C_{21}$; $C_{27}$; $C_{29}$; $C_{31}$ | $C_{24}$; $C_{25}$; $C_{27}$; $C_{29}$; $C_{31}$ | $C_{27}$; $C_{29}$; $C_{31}$ | $C_{23}$; $C_{27}$; $C_{29}$ |
| Aromatics | | | | | | |
| Average concentration, ng $m^{-3}$ | 0.2(S), 0.2(W) | 5.8(S), 21.9(W) | 0.3(S), 0.4(W) | 0.7(S), 1.4(W) | 0.8(S), 0.3(W) | 2.7(S), 38.9(W) |
| Maximum concentration, ng $m^{-3}$ | 0.8 (methylanthracenes) | 4.2 (benzo[e]pyrene) | 0.6 (methylanthracenes) | 0.6 (methylanthracenes) | 0.2 (benzo[a]anthracene) | 5.8 (fluoranthene) |
| *n*-alkanals | | | | | | |
| Average concentration, ng $m^{-3}$ | 1.2(S), 0.7(W) | 3.1(S), 8.0(W) | 7.1(S), 0.9(W) | 4.6(S), 0.7(W) | 0.9(S), 1.4(W) | 23.2(S), 14.7(W) |
| Maximum concentration, ng $m^{-3}$ | 1.4 ($C_{28}$) | 3.0 ($C_{22}$) | 8.6 ($C_{26}$) | 4.8 ($C_{26}$) | 1.0 ($C_{25}$) | 11.8 ($C_{28}$) |
| Carbon range | $C_{14}-C_{30}$ (dis.) | $C_{15}-C_{30}$ (dis.) | $C_{12}-C_{30}$ (dis.) | $C_{11}-C_{30}$ (dis.) | $C_{12}-C_{30}$ (dis.) | $C_{12}-C_{30}$ (dis.) |
| $C_{max}$ | $C_{26}$; $C_{28}$; $C_{30}$ | $C_{22}$; $C_{23}$; $C_{26}$; $C_{28}$ | $C_{26}$ | $C_{24}$;$C_{26}$ | $C_{14}$; $C_{15}$; $C_{25}$; $C_{26}$; $C_{28}$ | $C_{22}$; $C_{24}$; $C_{26}$; $C_{28}$ |
| *n*-alkanones | | | | | | |
| Average concentration, ng $m^{-3}$ | 0.2(S), 0.1(W) | 0.6(S), 0.2(W) | 0.3(S), 0.1(W) | 0.9(S), 0.3(W) | 0.3(S), 0.2 (W) | 3.4(S), 3.3 (W) |
| Maximum concentration, ng $m^{-3}$ | 1.2 ($C_{29}$) | 1.9 ($C_{29}$) | 0.3 ($C_{29}$) | 1.7 ($C_{29}$) | 0.3 ($C_{19}$) | 3.3 ($C_{28}$) |
| Carbon range | $C_{17}-C_{29}$ (dis.) | . . . | $C_{17}-C_{29}$ (dis.) | $C_{16}-C_{31}$ (dis.) | $C_{14}-C_{31}$ (dis.) | $C_{14}-C_{31}$ (dis.) |
| $C_{max}$ | $C_{27}$; $C_{29}$ | $C_{29}$ | $C_{25}$; $C_{29}$ | $C_{23}$; $C_{25}$; $C_{27}$; $C_{29}$ | $C_{15}-C_{17}$; $C_{19}$; $C_{21}-C_{23}$; $C_{29}$ | $C_{21}$; $C_{23}$; $C_{29}$; $C_{31}$ |
| *n*-alkanols | | | | | | |
| Average concentration, ng $m^{-3}$ | 3.7(S), 3.0(W) | 19.9(S), 25.2(W) | 26.9(S), 2.9(W) | 30.2(S), 3.7(W) | 11.1(S), 2.0(W) | 25.6(S), 45.2(W) |
| Maximum concentration, ng $m^{-3}$ | 7.1 ($C_{28}$) | 25.2 ($C_{26}$) | 36.0 ($C_{29}$) | 32.0 ($C_{26}$) | 9.9 ($C_{28}$) | 24.2 ($C_{26}$) |
| Carbon range | $C_{12}-C_{30}$ | $C_{12}-C_{30}$ | $C_{12}-C_{30}$ | $C_{12}-C_{30}$ | $C_{12}-C_{30}$ | $C_{12}-C_{30}$ |
| $C_{max}$ | $C_{26}$; $C_{28}$ | $C_{23}$; $C_{26}$ | $C_{26;}$; $C_{29}$ | $C_{24}$; $C_{26}$ | $C_{14}$; $C_{16}$; $C_{18}$; $C_{25}$; $C_{26}$; $C_{28}$ | $C_{12}$; $C_{26}$ |
| *n*-acids | | | | | | |
| Average concentration, ng $m^{-3}$ | 7.3(S), 1.3(W) | 25.2(S), 41.6(W) | 8.5(S), 4.4(W) | 14.8(S), 6.6(W) | 7.0(S), 6.5(W) | 79.3(S), 155.1(W) |
| Maximum concentration, ng $m^{-3}$ | 15.1 ($C_{22}$) | 18.4 ($C_{24}$) | 9.8 ($C_{16}$) | 5.4 ($C_{16}$) | 7.2 ($C_{16}$) | 50.8 ($C_{22}$) |
| Carbon range | $C_{9}-C_{30}$ | $C_{9}-C_{32}$ | $C_{8}-C_{30}$ | $C_{12}-C_{30}$ | $C_{7}-C_{30}$ | $C_{8}-C_{30}$ |
| $C_{max}$ | $C_{16}$; $C_{22}$; $C_{24}$ | $C_{16}$; $C_{24}$ | $C_{16}$ | $C_{16}$; $C_{22}$; $C_{24}$; $C_{26}$ | $C_{16}$; $C_{18}$ | $C_{16}$; $C_{22}$; $C_{24}$ |
| UCM | | | | | | |
| Average concentration, ng $m^{-3}$ | 0.7(S), 1.1(W) | 32.2(S), 126(W) | 8.5(S), 5.2(W) | 8.9(S), 6.2(W) | 25(S), 13.9(W) | 26.3(S), 66.7(W) |
| Maximum concentration, ng $m^{-3}$ | 4.4 | 276.7 | 15.0 | 13.9 | 74.4 | 131.0 |

[a]S, summer; W, winter; dis., discontinuous series.

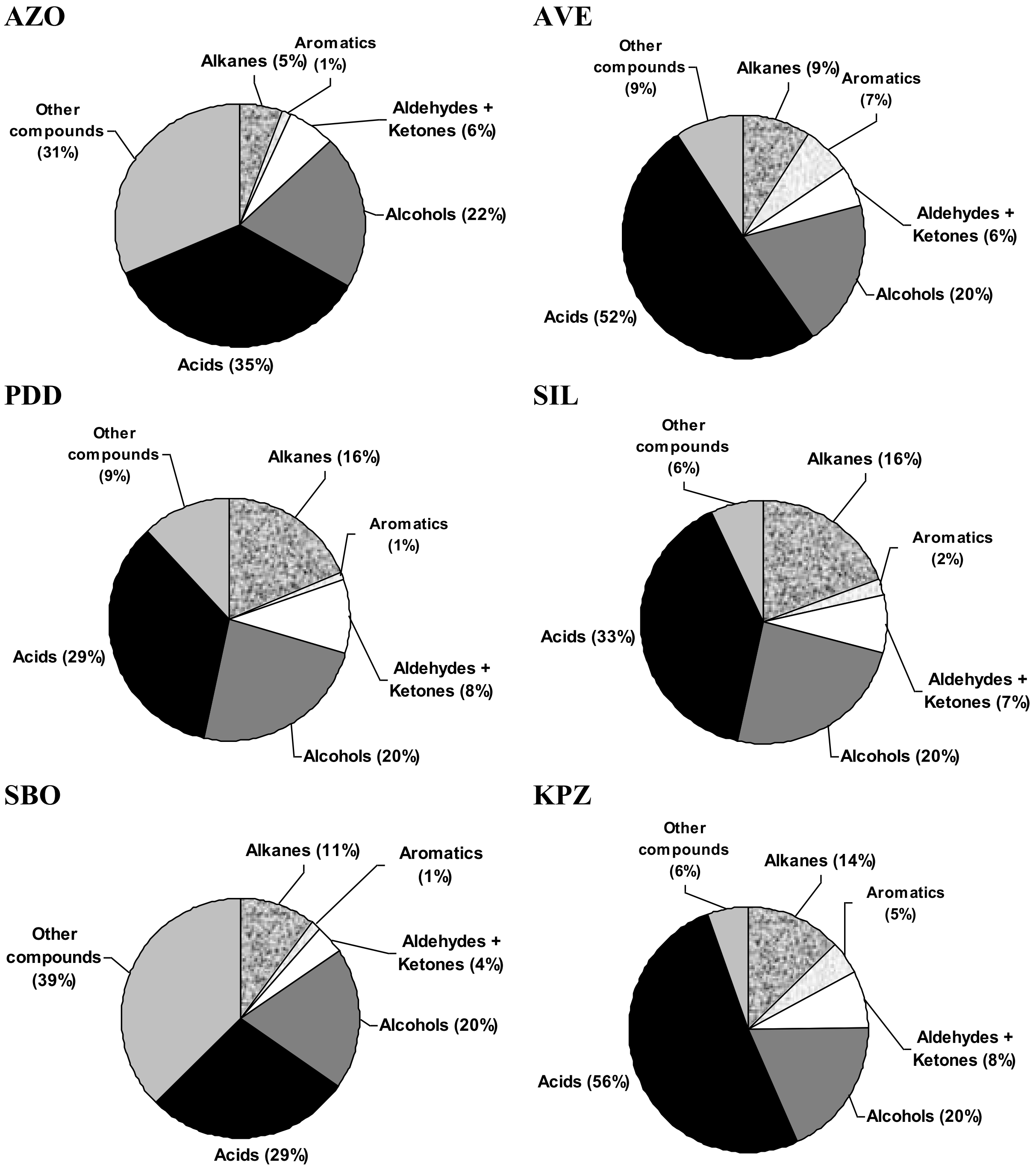


**Figure 1.** Contribution of different organic classes to the chromatographically identifiable organic compounds, showing the predominant contribution of acids, alkanes and alcohols to the resolved organics in aerosols from six nonurban sites.

from further petrogenic inputs. According to *Simoneit* [1989], diesel exhaust presents a relative maximum at $n$-$C_{23}$.

[13] The monthly averages of CPI and WNA are presented in Figure 2. CPI calculations indicate a significant anthropogenic influence throughout the entire sampling period in AVE (CPI < 3), and during winter for all other locations. The WNA reveal a more important contribution from vascular plants to the total $n$-alkanes during the warm season at all locations, probably because of the higher emissions from both deciduous and coniferous trees in summer. A lower annual average fractional contribution, approximately of 30%, is observed at AVE and SBO by comparison with values higher than 47% at the four other sites (Table 4). The stronger contribution of anthropogenic sources to the global amounts of $n$-alkanes in AVE and SBO is also indicated by the U:R ratio, which presents seasonal average values above 2.9 and below 2.4 for these two sites and for the remaining locations, respectively. Wood and coal combustion exhibit U:R values from 2.3 to 3.9,

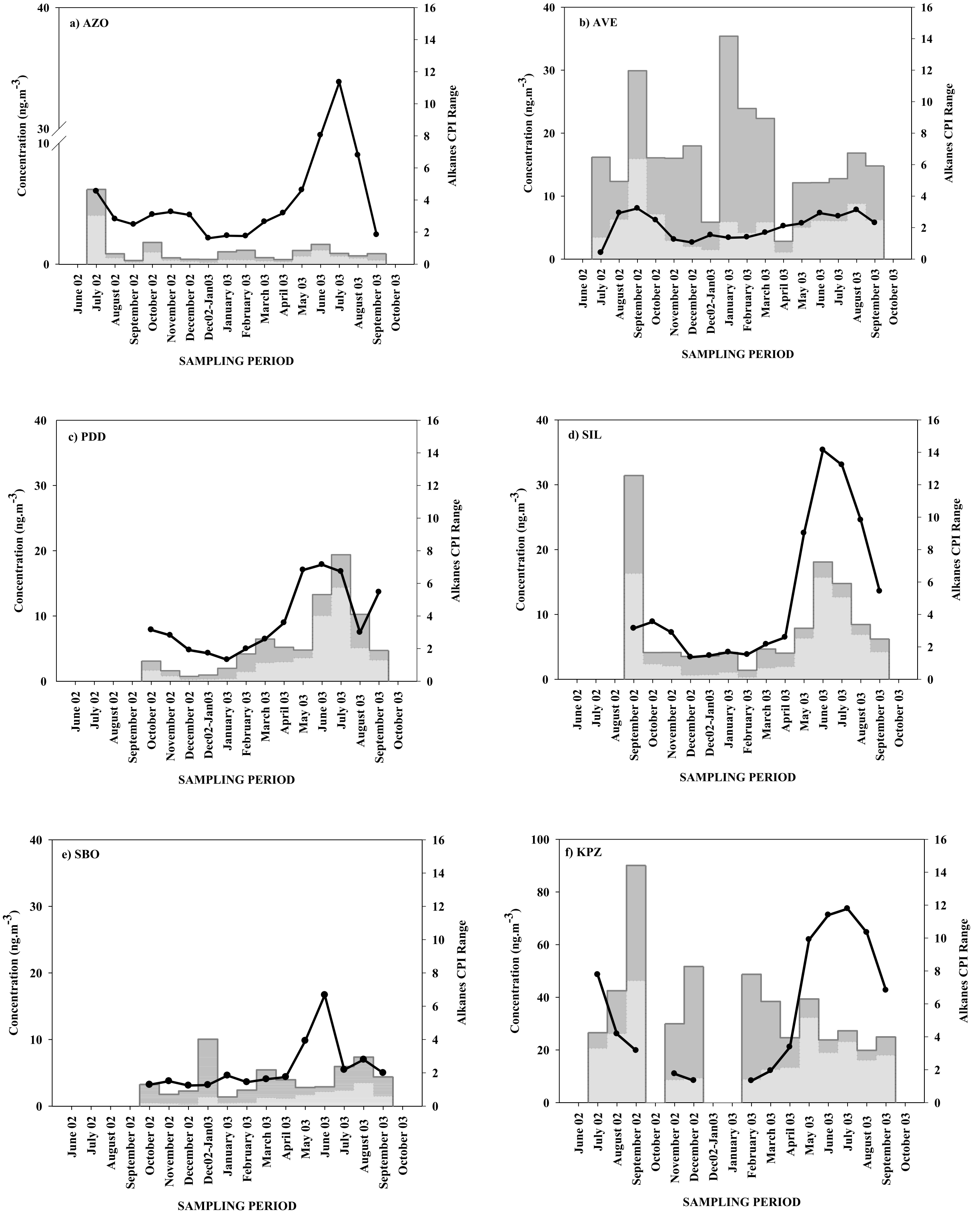


**Figure 2.** Monthly average concentrations of anthropogenic *n*-alkanes (dark grey), wax *n*-alkanes (light grey), and global CPI (black dotted line) in aerosols collected at the six CARBOSOL sites reflecting a more important contribution from vascular plants in the warm season.

whereas vehicular emissions result in values higher than 4.0 [*Tang et al.*, 2006]. Pure hydrocarbon mixtures from plant waxes have U:R < 0.1 [*Azevedo et al.*, 2002]. U:R values for rural, mixed and urban western United States samples, for example, are 0.2–4, 1.4–3.4 and 0.9–25, respectively [*Simoneit*, 1984]. Seasonally, while at SBO higher average U:R ratios were found during summer, at all other sites, maxima occurred during the winter period. It seems therefore that at SBO contamination from anthropogenic emissions occurred as a result of long-range transport from

**Table 4.** Summer and Winter Average Values for Geochemical Parameters Applied to Organic Classes in Aerosols From the Six CARBOSOL Sites[a]

| | AZO | AVE | PDD | SIL | SBO | KPZ |
|---|---|---|---|---|---|---|
| Organic class/season | S-W | S-W | S-W | S-W | S-W | S-W |
| *n*-alkanes | | | | | | |
| Global CPI | 5.1–2.5 | 2.5–1.5 | 5.5–2.2 | 8.2–2.1 | 3.2–1.5 | 7.6–1.6 |
| WNA, ng $m^{-3}$ | 0.9–0.4 | 6.8–4.2 | 6.5–1.1 | 9.1–1.2 | 2.0–0.6 | 23.8–9.8 |
| WNA, % | 57.8–42.8 | 44.8–22.5 | 66.2–36.9 | 71.5–31.9 | 46.8–18.8 | 71.4–24.3 |
| U:R | 1.0–1.7 | 2.9–7.8 | 1.2–2.1 | 0.9–2.4 | 5.0–3.8 | 1.4–1.8 |
| *n*-alkanols | | | | | | |
| Global CPI | 14.1–18.4 | 13.0–5.5 | 32.0–11.8 | 23.7–8.9 | 11.6–3.1 | 14.4–11.7 |
| WNAL, ng $m^{-3}$ | 3.6–3.3 | 17.0–16.0 | 23.4–2.4 | 29.2–2.9 | 7.9–0.9 | 20.6–31.4 |
| WNAL, % | 83.1–89.6 | 84.2–63.1 | 93.5–79.6 | 90.3–75.3 | 76.8–46.2 | 85.2–73.4 |
| *n*-carboxylic acids | | | | | | |
| Global CPI | 5.2–4.9 | 4.2–6.2 | 8.4–5.3 | 5.5–4.0 | 5.9–6.4 | 5.0–4.3 |
| WNAC, ng $m^{-3}$ | 5.7–0.9 | 16.1–27.5 | 8.5–2.8 | 10.3–3.9 | 5.6–4.6 | 44.1–93.3 |
| WNAC, % | 67.3–66.7 | 59.2–69.9 | 75.8–69.0 | 66.4–58.9 | 71.6–72.6 | 64.0–60.4 |
| Aromatics | | | | | | |
| CPAHs/TPAHs | 0.11–0.16 | 0.65–0.65 | 0.54–0.72 | 0.43–0.73 | 0.46–0.71 | 0.64–0.66 |
| MP/P | n.d. | 1.03–2.51 | 3.45–2.75 | n.d.–0.25 | n.d. | 4.61–2.52 |
| BeP/(BeP + BaP) | 1.00–0.89 | 0.66–0.63 | 0.91–0.75 | 0.93–0.93 | n.d. | 0.83–0.63 |
| Fl/(Fl + Py) | 1.00–1.00 | 0.45–0.49 | 0.61–0.60 | 0.59–0.56 | n.d.–0.83 | 0.54–0.53 |
| IP/(IP + BgP) | 0.48–0.49 | 0.41–0.41 | 0.46–0.49 | 0.35–0.43 | n.d.–0.45 | 0.42–0.46 |
| BA/(BA + CT) | n.d. | 0.36–0.46 | n.d.–0.62 | 0.53–0.36 | n.d.–0.61 | 0.57–0.39 |

[a] n.d., not defined; CPAHs, nine combustion PAH (fluoranthene, pyrene, benzo[a]anthracene, crysene, benzofluoranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno[1, 2, 3-cd-pyrene] and benzo[ghi]perylene); TPAHs, total concentration of PAHs; MP, methylphenanthrenes; P, phenanthrene; BeP, benzo[e]pyrene; BaP, benzo[a]pyrene; Fl, fluoranthene; P, pyrene; IP, indeno[1, 2, 3-cd]pyrene; BgP, benzo[ghi]perylene; BA, benzo[a]anthracene; CT, chrysene and triphenylene.

polluted areas through injection of boundary layer contaminated air at high tropospheric levels. Another hypothesis is the contamination of the local atmosphere by construction works during the warmer months.

[14] Petroleum molecular markers are specific indicator compounds mainly present in the hydrocarbon fractions. These kind of tracers may include the 17$\alpha$(H), 21$\beta$(H)-hopane series, the 5$\alpha$(H), 14$\alpha$(H), 17$\alpha$(H) and 5$\alpha$(H), 14$\beta$(H), 17$\beta$(H)-sterane series, as well as the isoprenoids pristane and phytane [*Gogou et al.*, 1996; *Simoneit*, 1984, 1999; *Simoneit et al.*, 1991; *Azevedo et al.*, 2002]. Pristane and phytane result from the diagenesis of phytol and are not primary components of the majority of terrestrial living organisms [*Simoneit*, 1984]. The presence of hopanes, steranes and isoprenoids in aerosols confirm an input source from fossil fuel utilization, especially by vehicular traffic [*Gogou et al.*, 1996; *Simoneit*, 1984, 1999; *Azevedo et al.*, 2002]. It should be noted, however, that the identification of compounds such as pristane and phytane in atmospheric samples are dependent on the sampling period. *Simoneit et al.* [2004] referred to the volatile compound blow-off from the filters over a 1–2 day acquisition time and the consequent depletion of aliphatics $<C_{21}$, and therefore of the petroleum tracers. In this study, the resultant weekly samples presented petroleum molecular markers only in samples from the Portuguese sampling sites. The presence of ramified hydrocarbons like pristane (Pr) and phytane (Ph) is consistent with fossil fuel sources of carbon in the interval $C_{16}$–$C_{20}$, which is approximately the distillation range of diesel fuels [*Abas and Simoneit*, 1996; *Zheng et al.*, 1997]. The total average concentrations of Pr and Ph ranged from 10 to 40 pg $m^{-3}$ and from 7 to 38 pg $m^{-3}$, respectively. Much higher concentrations of these hydrocarbons (68.3 and 64.5 ng $m^{-3}$) were found in southern California during a severe photochemical smog episode [*Fraser et al.*, 1997], but also over a Portuguese rural area (<15 and <19 ng $m^{-3}$) [*Pio et al.*, 2001b]. Biogenic inputs are often dominated by a predominance of the odd carbon alkanes and the $C_{17}$ isoprenoid (pristane). Since phytane is rarely found in biological material (except some bacteria), most biological hydrocarbons have a Pr/Ph ratio $\gg 1.0$. The Pr/Ph ratios ranged from 0.21 to 5.60 in AZO and from 0.45 to 1.74 in AVE. Values approaching the unity for AVE indicate a hydrocarbon signature derived from petrochemical use, analogous to others described for urban aerosols. The 17$\alpha$(H), 21$\beta$(H)-hopanes were only detected in AVE, and mainly during the winter period (Table 5). The series presented the typical 22S:R pairs and maximize at $C_{29}$. Concentrations of the 22S hopanes were always higher than those for the corresponding 22R pairs. This type of distribution is commonly found in aerosols emitted by gasoline and diesel engines. Biogenic precursors contain only the 22R 17$\beta$(H), 21$\beta$(H)-hopane configuration [*Peters and Moldowan*, 1993; *Peters et al.*, 2005].

### 3.2.2. Aromatic Hydrocarbons

[15] PAHs detected in samples from the six nonurban European sites ranged from phenanthrene to coronene, with individual levels never exceeding 5.8 ng $m^{-3}$. This maximum concentration was obtained for fluoranthene in KPZ during February 2002. This concentration is two to six times higher than the maximum levels measured in Greek (2.0 ng $m^{-3}$) [*Gogou et al.*, 1996], Swedish (3.0 ng $m^{-3}$) and Finnish (0.7 ng $m^{-3}$) rural areas [*Prevedouros et al.*, 2004]. The average concentrations of total PAHs are higher at the continental low-level sites of AVE and KPZ, which present levels comparable to those from Algiers City (14.7 ng $m^{-3}$ [*Yassaa et al.*, 2001]) and from an urban area of Birmingham during winter (18.1 ng $m^{-3}$ [*Smith and Harrison*, 1996]). The average concentrations measured for KPZ are more than 20 times higher than the results obtained for AZO, PDD, SIL and SBO (Table 3). The results obtained for these four locations are in the range of

**Table 5.** Seasonal Average Concentrations of Molecular Markers in Aerosols From the CARBOSOL Sampling Sites[a]

| Compound | Season | AZO | AVE | PDD | SIL | SBO | KPZ |
|---|---|---|---|---|---|---|---|
| Retene | summer | . . . | 71.68 | 6.92 | . . . | . . . | . . . |
| Retene | winter | . . . | 654.85 | 14.32 | . . . | . . . | . . . |
| Campesterol | summer | . . . | 134.35 | 106.69 | 89.41 | 66.03 | 121.01 |
| Campesterol | winter | . . . | 438.94 | 20.36 | 15.58 | 7.14 | 551.98 |
| Stigmasterol | summer | 4.45 | 232.78 | . . . | . . . | . . . | . . . |
| Stigmasterol | winter | 24.15 | 935.64 | . . . | . . . | . . . | . . . |
| $\beta$-sitosterol | summer | 29.88 | 424.98 | 683.72 | 409.87 | 232.00 | 432.66 |
| $\beta$-sitosterol | winter | 19.29 | 1371.70 | 114.88 | 78.71 | 70.48 | 1306.99 |
| Cholesterol | summer | 30.44 | 91.35 | 133.24 | 174.44 | 61.16 | 87.65 |
| Cholesterol | winter | 23.53 | 280.93 | 37.01 | 25.44 | 74.16 | 93.00 |
| 7-oxodehydroabietic acid | summer | 36.31 | 4743.99 | 171.88 | 279.14 | 126.82 | 803.47 |
| 7-oxodehydroabietic acid | winter | 30.14 | 16299.71 | 194.05 | 524.44 | 119.51 | 3521.65 |
| Dehydroabietic acid | summer | 23.44 | 7857.85 | 414.77 | 436.77 | 72.77 | 1862.71 |
| Dehydroabietic acid | winter | 30.24 | 89407.15 | 446.28 | 801.84 | 282.73 | 14686.59 |
| Pimaric acid | summer | . . . | 44.95 | 33.43 | . . . | . . . | 143.61 |
| Pimaric acid | winter | . . . | 1301.23 | 38.12 | . . . | 11.00 | . . . |
| Isopimaric acid | summer | . . . | 51.36 | 12.44 | . . . | . . . | . . . |
| Isopimaric acid | winter | . . . | 1236.51 | 28.00 | . . . | 25.47 | . . . |
| Sandaracopimaric acid | summer | . . . | 335.78 | 16.00 | 30.64 | 7.90 | . . . |
| Sandaracopimaric acid | winter | . . . | 4095.46 | 11.90 | . . . | 35.68 | . . . |
| 6, 10, 14-trimethylpentadecan-2-one | summer | 263.37 | 4.17 | 82.75 | 5.71 | 244.24 | 459.04 |
| 6, 10, 14-trimethylpentadecan-2-one | winter | 200.22 | 8.27 | 19.48 | 10.03 | 71.11 | 289.08 |
| Pristane | summer | 12.13 | 38.48 | . . . | . . . | . . . | . . . |
| Pristane | winter | 4.75 | 42.69 | 0.21 | . . . | . . . | . . . |
| Phytane | summer | 6.52 | 39.98 | . . . | . . . | . . . | . . . |
| Phytane | winter | 7.47 | 36.13 | . . . | . . . | 6.69 | . . . |
| Octadecanoic acid ($C_{18:0}$) | summer | 636.09 | 3293.67 | 1554.91 | 2117.89 | 1250.53 | 6511.33 |
| Octadecanoic acid ($C_{18:0}$) | winter | 208.41 | 3956.49 | 583.64 | 860.57 | 1914.91 | 13518.29 |
| Oleic acid ($C_{18:1}$) | summer | 259.00 | 462.27 | 1371.20 | 1795.67 | 1445.31 | 1782.31 |
| Oleic acid ($C_{18:1}$) | winter | 75.01 | 568.78 | 207.52 | 231.12 | 266.39 | 5660.45 |
| Linoleic acid ($C_{18:2}$) | summer | 136.49 | 240.54 | 1826.82 | 1367.13 | 833.69 | 2132.48 |
| Linoleic acid ($C_{18:2}$) | winter | 25.38 | 367.41 | 51.12 | 49.58 | 66.22 | 955.09 |
| Palmitoleic acid ($C_{16:1}$) | summer | 51.84 | . . . | 35.44 | 323.06 | 47.55 | . . . |
| Palmitoleic acid ($C_{16:1}$) | winter | 27.19 | . . . | 9.43 | 1.92 | 15.04 | . . . |

[a] Unit is pg $m^{-3}$.

those reported for rural and urban U.S. west coast areas (0.01–2.2 ng $m^{-3}$ [*Simoneit*, 1984]), and for a rural area in Birmingham during summer (1.02 ng $m^{-3}$ [*Smith and Harrison*, 1996]). Higher average concentrations are found during winter for AVE, PDD, SIL and KPZ, and during summer for the site under upslope weather conditions (SBO). At AZO, with mild climate all year, no marked seasonality is observed (Table 3). Higher PAH levels are generally observed in winter as a consequence of an increase in wood burning and in consumption of fossil fuel combustibles, lower losses due to photochemical degradation and the fact that meteorological conditions during this period (i.e., more frequent and lower temperature inversions) are less favorable for pollutant dispersion [*Kalaitzoglou et al.*, 2004].

[16] Retene, a completely dehydrogenated resin diterpenoid also detected, is a pyrolysis end product from diterpenoids that have the abietane or pimarane skeletons. It has been proposed as molecular tracer for coniferous wood [*Simoneit and Mazurek*, 1982; *Simoneit*, 1999, 2002]. It is known that the burning conditions have an impact on this biomarker: in an oxygen-sufficient and high-temperature environment, less retene is expected because of thermal cracking, while the opposite conditions promote its formation [*Fang et al.*, 1999]. Retene was only detected in AVE and PDD with average concentrations between 0.01 ng $m^{-3}$ and 0.33 ng $m^{-3}$, and presenting higher values during the winter period. The contribution of retene to the total measured organic concentration did not surpass, on average, 0.30%. Although AVE and PDD showed average concentrations of retene below the low end of the range (6–8 ng $m^{-3}$) measured for cities where wood is used for heating in 50% or more of all households [*Ramdahl*, 1983], similar levels were observed in some rural and urban areas of Mississippi, Georgia and Florida [*Zheng et al.*, 2002].

[17] Further assessment of processes affecting the composition of hydrocarbons can be obtained from concentration ratios between different PAH species [*Pio et al.*, 2001b]. These parameters must be used with caution because they assume only minor modifications following emission and no sampling artifacts (especially in the case of the reactive benzo[a]pyrene) [*Gogou and Stephanou*, 2000]. During the CARBOSOL campaign, weekly sampling did not include special devices, such as diffusion denuders and foam plugs. Therefore volatilization losses or adsorption artifacts may have occurred on the filter for semivolatile organic constituents, especially for the low molecular weight compounds because of their high volatility [*Kavouras et al.*, 1999]. The mean values of the sum of nine combus-

tion nonalkylated compounds to the total concentrations of PAHs (CPAHs/TPAHs) were generally higher than 0.50 (Table 4), excepting for the background oceanic site (AZO). The higher ratio values observed, suggest that a large fraction of PAHs originated from pyrogenic sources, rather than from fossil fuel volatilization [*Alves*, 2001]. Methylphenanthrenes and phenanthrene were absent from samples of the AZO and SBO sites throughout the campaign, while at SIL they were detected only in summer. The mean MP/P ratios in AVE, PDD and KPZ are higher than 1, indicating a predominance of petrogenic emissions (e.g., vehicular exhausts), rather than stationary combustion sources [*Gogou et al.*, 1996; *Tsapakis et al.*, 2002]. The BeP/(BeP + BaP) is affected by the strong reactivity in the atmosphere, since benzo[a]pyrene is easily decomposed by light and oxidants. Most of the fresh exhausts have similar contents of benzo[e]pyrene and benzo[a]pyrene, thus the increase of the ratio can be regarded as an index of the aging of particles [*Tsapakis et al.*, 2002]. The mean values obtained for this ratio suggest fresher emissions during the entire sampling period in AVE and during winter at KPZ (values close to 0.50). The summer periods present, in general, higher ratios, indicating more intense photochemical or thermal reactions with ozone, nitric oxides and hydroxyl radicals. The mean Fl/(Fl + Py) ratios in CARBOSOL sites are in the range 0.5–0.8. These values are similar to those previously published for vehicular emissions [*Rogge et al.*, 1993a]. The IP/(IP + BgP) ratio is normally used to distinguish between vehicular emissions and stationary sources (including wood and coal domestic heating). Similar IP/(IP + BgP) ratios were obtained in all CARBOSOL sites (0.35–0.49), with higher values usually during winter. A comparison of these values to those previously published (0.18 for cars, 0.37 for diesel, 0.56 for coal [*Grimmer et al.*, 1983], and 0.62 for wood smoke impacted aerosols [*Gogou et al.*, 1996]) indicates that the importance of mobile source contributions may be surpassed by the stationary inputs during the wintry months, because of the probable increase in domestic wood burning. The mean Ba/(Ba + CT) ratio presents values between 0.36 and 0.61, which are similar to those calculated for oil combustion sources, such as vehicles [*Tsapakis et al.*, 2002]. Overall, the PAH concentration diagnostic ratios estimated for the CARBOSOL sites suggest that aromatic compounds are associated with a variety of stationary and mobile (e.g., vehicular) sources, hinting a predominance of wood burning emissions in winter. The low-level continental sites are the most affected by petrogenic and pyrogenic emission sources.

### 3.2.3. Aldehydes and Ketones

[18] Atmospheric particulate *n*-alkanals and *n*-alkanones with less than 20 carbons result predominantly from oxidative processes, anthropogenic activities, or microbial action over alkanes, alkenes or other constituents [*Simoneit et al.*, 1988; *Stephanou and Stratigakis*, 1993]. Compounds with higher molecular weights may occur in the epicuticular waxes as a result of the reaction of $O_3$ on unsaturated hydrocarbons [*Alves*, 2001]. In CARBOSOL samples, the homologous series of *n*-alkanals ranged from $C_{11}$ to $C_{30}$, presenting average total concentrations between 1.0 ng m$^{-3}$ (AZO and SBO) and 19.0 ng m$^{-3}$ (KPZ). Excepting for AVE, levels are higher in summer than in winter (Table 3). In general, all CARBOSOL sites present *n*-alkanals with maximum concentrations for compounds with chain lengths above $C_{22}$ during the entire sampling period, indicating an origin in particulate abrasion products from leaf surfaces and biomass burning. The only exception occurred during winter in SBO, where $C_{14}$ and $C_{15}$ became prevalent, in accordance with a local significant microbial source throughout this season [*Simoneit et al.*, 1988; *Stephanou and Stratigakis*, 1993]. The homologous distributions of *n*-alkan-2-ones varied between $C_{14}$ and $C_{31}$ for almost all locations. The single exception occurred in AVE, where only the $C_{29}$ ketone was detected. The average concentrations of total *n*-ketones ranged between 0.2 ng m$^{-3}$ (AZO and PDD) and 3.4 ng m$^{-3}$ (KPZ), presenting higher values during summer (Table 3). Geochemical parameters for the carbonyl families are not presented because of the discontinuity of the homologous series during the sampling period, at all locations.

[19] One of the predominant ketones found in the atmospheric aerosol samples was the phytone (6, 10, 14-trimethylpentadecan-2-one). It is produced by thermal alteration and oxidation of phytol, which is part of the chlorophyll molecule, and has been proposed as a marker for secondary biogenic aerosol [*Brown et al.*, 2002; *Gogou et al.*, 1996; *Pio et al.*, 2001b; *Simoneit et al.*, 1988]. This isoprenoid compound has been previously detected in rural aerosols from Crete [*Gogou et al.*, 1996], Portugal [*Pio et al.*, 2001b], Big Bend National Park, Texas [*Brown et al.*, 2002] and rural Nigeria [*Simoneit et al.*, 1988] at levels ranging between values close to 1 and dozens of ng m$^{-3}$. The small coastal city of AVE and the forested mountain site of SIL received rather low concentrations of this isoprenoid ketone throughout the year and, inclusively, it was absent from some samples. The Atlantic background site of AZO and the Hungarian plains of KPZ presented the highest levels. Aside from the two sites where the ketone is not noteworthy, the seasonal variation of phytone showed higher concentrations during the summer months. The wintry decrease suggests that secondary aerosol formation from biomass degradation may be less important in these sample composites [*Brown et al.*, 2002].

### 3.2.4. Alcohols and Sterols

[20] In aerosols from the CARBOSOL sites, the typical distributions of *n*-alkanols ranged from $C_{12}$ to $C_{30}$ with a strong even-to-odd carbon number predominance, reflecting a prevailing biogenic origin (Tables 3 and 4 and Figure 3). In opposition to the higher molecular weight compounds, the homologues $<C_{20}$ are not in fresh vascular plant waxes and may have a microbial origin [*Alves et al.*, 2001]. The average concentrations varied from 3.4 ng m$^{-3}$ (AZO) to 35.4 ng m$^{-3}$ (KPZ). By contrast with the other locations, AVE and KPZ present higher concentrations during winter. This may reflect an enhanced microbial and/or anthropogenic component during the colder season, since the wax constituents have a smaller percentage contribution to the aerosol content in this period of the year compared to the summer time. The WNAL comprise the majority of the mass of the homologous series, representing up to 94%. The highest concentrations of WNAL are observed in summer (Table 4), reflecting some seasonality of wax production.

[21] Phytosterols consist of sterols of higher photosynthetic plants originated by a biosynthetic pathway of cycli-

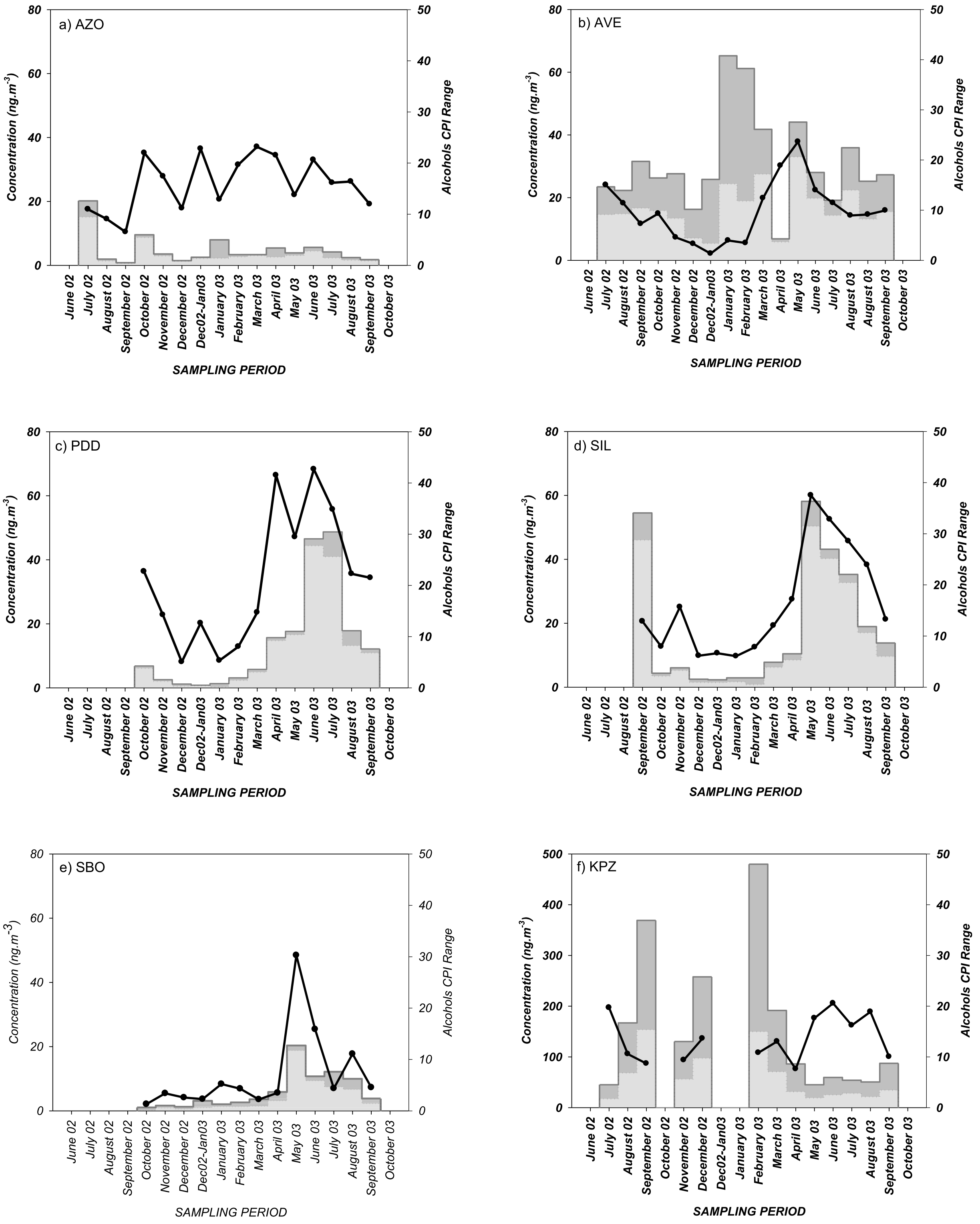


**Figure 3.** Monthly average concentrations of anthropogenic (dark grey) and wax *n*-alkanols (light grey) and global CPI (black dotted line) evaluation in aerosols from CARBOSOL sites, showing a major contribution of leaf epicuticular constituents of the vegetation.

zation, where squalene is the precursor [*Simoneit et al.*, 1991]. Whereas $\beta$-sitosterol ($C_{29}$) and stigmasterol ($C_{29}$) are indicators for vegetation in general, campesterol ($C_{28}$) has been pointed out as a specific molecular tracer for gramineae [*Simoneit*, 2002; *Oros and Simoneit*, 1999]. In this study, campesterol was not detected in AZO, and stigmasterol was present only in the Portuguese sampling sites. *Pio et al.* [2001b] report that the absence of campesterol might be due to its degradation toward other compounds, or as a result of its absence from the vegetation waxes affecting the aerosol composition. Cholesterol ($C_{27}$) is an important constituent of cell membranes found in animal tissues. It has been proposed as a molecular marker of meat frying and grilling operations [*Nolte et al.*, 1999]. However, this $C_{27}$ sterol should not be viewed as an unique tracer for emissions during meat cooking, since it was also detected in pine, oak and eucalyptus wood smoke [*Nolte et al.*, 2001]. *Simoneit and Elias* [2000] report that the presence of cholesterol in oceanic aerosols probably indicates an input from marine sources such as algae, which also can contribute to continental cholesterol sources in environments downwind from lacustrine areas.

[22] Different carbon number distributions have been obtained in distinct experiments, suggesting that the phytosterol patterns may be related to geographical characteristics, particularly the specific plant communities and the climatic conditions [*Pio et al.*, 2001b; *Simoneit*, 1989; *Simoneit et al.*, 1988, 1990]. The sterol carbon number distributions, considering the total average concentrations, reveal similar patterns for AVE and KPZ with $C_{29} > C_{28} > C_{27}$, while at the continental higher mountain sites (PDD, SIL and SBO) a distribution of $C_{29} > C_{27} > C_{28}$ was evident. AZO reveals a sterol distribution with $C_{29} > C_{27}$. The pattern found in PDD, SIL and SBO is similar to that reported by *Simoneit et al.* [1988] for aerosol samples from Nigeria and for the Amazon region [*Simoneit et al.*, 1990]. This distribution correlates with the predominance of wax components from vegetation and also from grass [*Simoneit et al.*, 1988]. Like in AZO, in a Portuguese semirural area, the $C_{28}$ phytosterol was not present at detectable levels, but an opposite pattern was reported with $C_{27} > C_{29}$ [*Pio et al.*, 2001b]. In general, while AVE and KPZ present higher average concentrations for all the identified sterols during the cold season, all other locations show higher levels during summer (Table 3). The distinct seasonality between elevated and surface continental sites is possibly a consequence of emission and transport. The seasonal pattern might indicate the predominance of vegetation waxes exudations in more remote sites, biomass burning and probably meat cooking operations as predominant sources in AVE and KPZ. Concentrations at the elevated sites are likely related to the effective decoupling of the lower layers from the midtroposphere during the cold season and to a more efficient upward transport of air masses from the boundary layer in summer than in winter.

### 3.2.5. Acids

[23] Fatty acids represent another major group of solvent-extractable compounds present in the aerosol phase. The distribution patterns ranged from $C_7$ to $C_{32}$, comprising saturated and unsaturated homologues. Depending on the site, a modal or bimodal distribution was observed, maximizing at $n$-$C_{16}$ and/or $n$-$C_{22}$-$n$-$C_{24}$. Alkanoic acids homologues > $n$-$C_{20}$ are constituents of vegetation waxes. Compounds with lower chain lengths can be derived from microbial sources [*Alves et al.*, 2001]. Moreover, *n*-alkanoic acids < $C_{18}$ also originate from biomass burning, food preparation, vehicle exhaust and tire wear debris [*Rogge et al.*, 1991, 1993c]. The annual average concentrations for the whole members of the homologous series ranged from a minimum of 4.3 ng m$^{-3}$ in the Atlantic site (AZO) to an upper limit of 117.2 ng m$^{-3}$ in KPZ. As verified for other compounds, at the two continental low-elevation sites concentrations maximize during winter, whereas an opposite tendency is observed at other locations (Table 3). CPI values >4 and a contribution from wax components higher than 60% are indicative that *n*-carboxylic acids are mainly derived from biogenic sources (Table 4).

[24] Unsaturated *n*-fatty acids (alkenoic acids) are emitted to the atmosphere from microbial sources and from the processing, degradation and combustion of plant and animal constituents [*Rogge et al.*, 1993b]. Meat cooking is an important source of *n*-alkenoic acids, mainly oleic ($C_{18:1}$) and palmitoleic acid ($C_{16:1}$) [*Rogge et al.*, 1991]. Phytoplankton and bacteria also contain a number of unsaturated fatty acids [*Rogge et al.*, 1993b; *Simoneit et al.*, 2004]. Biomass burning presents, in general, as primary components palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acids [e.g., *Oros and Simoneit*, 1999]. Once emitted into the atmosphere, unsaturated fatty acids, which are indicators of recent biogenesis [*Simoneit et al.*, 1991], are likely to be attacked by free radicals, ozone and other oxidants, producing aldehydes, lower-weight carboxylic acids and dicarboxylic acids [*Rogge et al.*, 1993b]. In this study, oleic and linoleic acids were detected in almost all occasions in all sampling sites. Total average concentrations ranged between 0.20 ng m$^{-3}$ (AZO) and 3.72 ng m$^{-3}$ (KPZ) for oleic acid and between 0.08 ng m$^{-3}$ (AZO) and 1.54 ng m$^{-3}$ (KPZ) for linoleic acid. Palmitoleic acid was measured in almost all occasions in AZO, occasionally in PDD, SIL and SBO, and never in AVE and KPZ. The total average concentration reached 0.16 ng m$^{-3}$ in SIL, 0.040 ng m$^{-3}$ in AZO, 0.031 ng m$^{-3}$ in SBO, and 0.022 ng m$^{-3}$ in PDD. Seasonally, the average levels were higher during summer for the more remote locations (AZO, PDD, SIL and SBO) and during winter for AVE and KPZ, suggesting a strong contribution of wood burning and/or meat cooking from October to March at these two sites (Figure 4). The concentration levels measured for oleic and linoleic acids are comparable to those of remote, rural and suburban areas in the United States [*Brown et al.*, 2002; *Zheng et al.*, 2002]. Values obtained for palmitoleic acid are lower than those measured in remote, rural and suburban areas in the United States and in the western north Pacific [*Zheng et al.*, 2002; *Simoneit et al.*, 2004].

[25] One method that has been used to gauge the age of aerosol is to take the ratio between the concentrations of the saturated $C_{18}$ alkanoic acid ($C_{18:0}$) and the monounsaturated $C_{18}$ acid ($C_{18:1}$). This ratio is used as an aerosol age indicator since the monounsaturated acid breaks down much faster by atmospheric oxidation than the saturated analogue. The abundance of the saturated acid compared to the monounsaturated homologue can, therefore, indicate a relative decomposition rate [*Brown et al.*, 2002]. The $C_{18:0}$/$C_{18:1}$ ratio measured during the CARBOSOL experiment presents successively decreasing averages for AVE (7.91), KPZ (6.28), SBO (4.27), SIL (3.45), AZO (2.75) and PDD (2.27). *Simoneit et al.* [1991] reported a noticeable increase of this ratio with increasing height above ground in Chinese urban areas. An opposite pattern was observed for the CARBOSOL samples during summer, showing an apparent

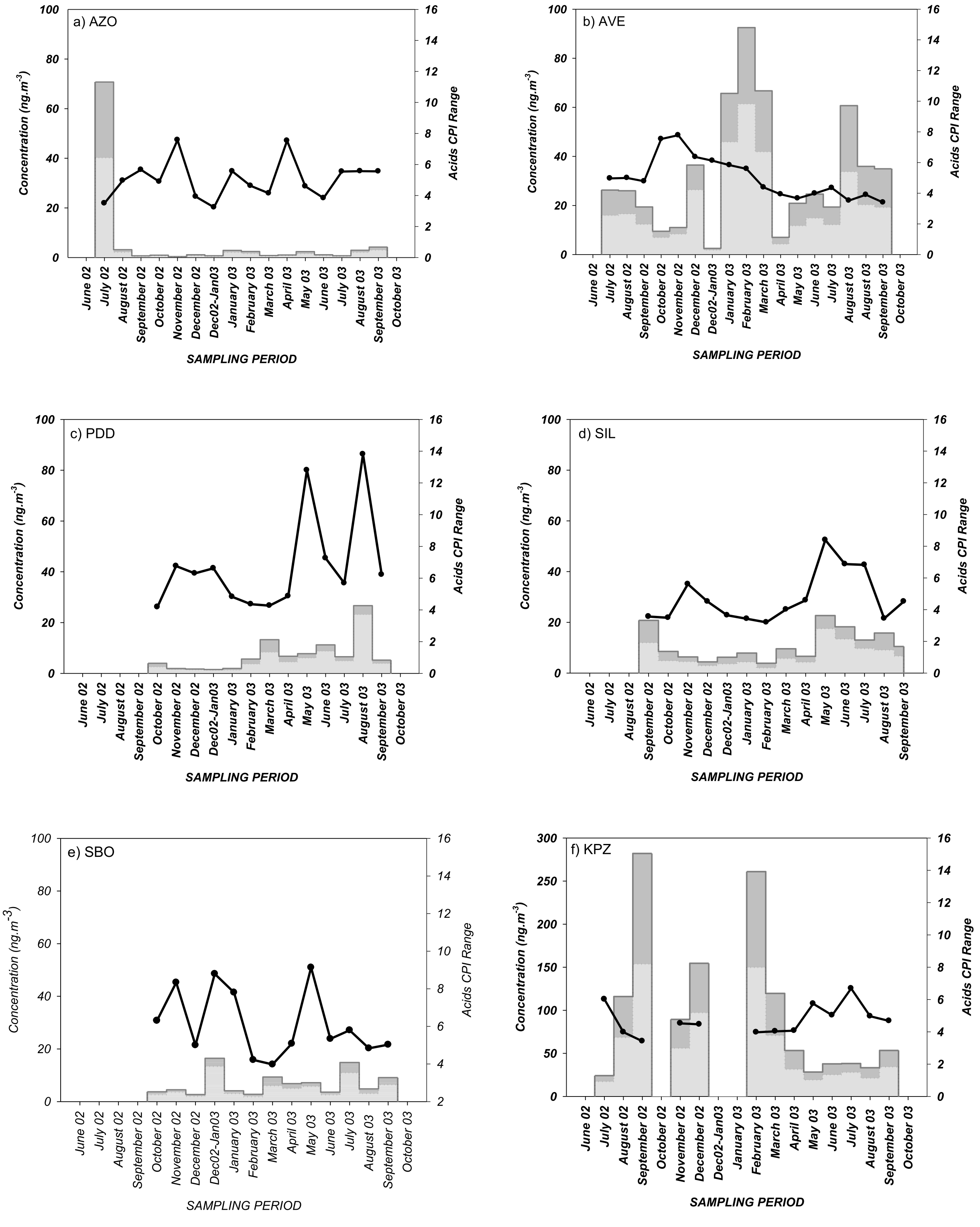


**Figure 4.** Monthly average concentrations of anthropogenic *n*-acids (dark grey), wax *n*-acids (light grey), and global CPI (black dotted line) values in aerosols from CARBOSOL sites showing higher concentrations during winter possibly due to biomass burning at the two continental low-elevation sites and global CPI values characteristic of a predominant biogenic origin.

enhancement with declining height. However, this correlation is not observable in the winter time. Similar results to AVE and KPZ were reported between 5 and 11 with an average of 6.6 for rural samples collected in remote Big Bend National Park, Texas. These high, rural-like ratios were ascribed to a combination of local rural biogenic emissions and aged aerosol advected from urban areas [*Brown et al.*, 2002]. Seasonally, the $C_{18:0}/C_{18:1}$ ratio

**Table 6.** Seasonal Averages for the Ratios Between $C_{18}$ and $C_{16}$ Fatty Acids

| Ratio | Season | AZO | AVE | PDD | SIL | SBO | KPZ |
|---|---|---|---|---|---|---|---|
| Octadecanoic acid ($C_{18:0}$)/oleic acid ($C_{18:1}$) | winter average | 3.26 | 8.13 | 2.82 | 4.59 | 6.41 | 7.61 |
| Octadecanoic acid ($C_{18:0}$)/oleic acid ($C_{18:1}$) | summer average | 2.23 | 7.69 | 1.71 | 2.31 | 2.13 | 4.94 |
| Octadecanoic acid ($C_{18:0}$)/hexadecanoic acid ($C_{16:0}$) | winter average | 0.55 | 0.55 | 0.60 | 0.89 | 0.86 | 0.49 |
| Octadecanoic acid ($C_{18:0}$)/hexadecanoic acid ($C_{16:0}$) | summer average | 0.79 | 0.80 | 0.60 | 0.69 | 0.55 | 0.60 |
| Octadecanoic acid ($C_{18:0}$)/linoleic acid ($C_{18:2}$) | winter average | 8.21 | 10.77 | 11.40 | 17.36 | 28.92 | 14.15 |
| Octadecanoic acid ($C_{18:0}$)/linoleic acid ($C_{18:2}$) | summer average | 4.66 | 13.69 | 0.85 | 1.55 | 1.50 | 3.05 |

presented higher averages during winter than summer for all studied locations, suggesting that the aerosols were more aged in colder periods that those of summer (Table 6). Except for AVE, the significant increase of the $C_{18:0}/C_{18:2}$ ratios in the winter samples confirms the existence of more aged air masses with relatively long residence time since their formation during the colder months [*Fang et al.*, 1999]. This suggests the superimposition of long-distance transport on local characteristics, rather that photochemical decomposition of unsaturated acids.

[26] While stearic and palmitic acids are, as individual compounds, not source specific, the $C_{18:0}/C_{16:0}$ fatty acid ratio is unique and can be used in source apportionment studies. The major contributors for particulate matter have $C_{18:0}/C_{16:0}$ ratios ranging from 0.17 to 0.71, depending on source type. In countries where dried cattle dung is used for cooking purposes, fine particulate smoke presents the characteristically elevated ratio around 2, whereas for foliar vegetation or wood smoke and car exhaust, values below 0.5 are typical. The surface soil and dusts from feedlots and open lot dairy farms showed an average $C_{18:0}/C_{16:0}$ ratio of 3.0 [*Rogge et al.*, 2006]. The fine particulate matter from CARBOSOL sites presented average ratios ranging from 0.55 to 0.89. Curiously, the elevated mountain sites showed higher values during the winter period, while at the low-level sites summer maxima dominated the seasonal variation. Values between 0.5 and 1 were also found in agricultural fields, dust from paved and unpaved roads and in $PM_{2.5}$ of rural and urban sources, such as hamburger charbroiling [*Rogge et al.*, 2006, and references therein].

[27] Resin acids, which are biosynthesized mainly by gymnosperms (e.g., pine and spruce) in temperate regions [*Rogge et al.*, 1998; *Simoneit*, 2002], were found in significant concentrations. They include unaltered (pimaric, isopimaric and sandaracopimaric acids) and thermal degradation products (dehydroabietic and 7-oxodehydroabietic acids). While the thermal degradation acids were found during almost all the sampling period at the different locations, the unaltered acids were more often detected in AVE and PDD (Table 6). The seasonal concentration of these resin constituents is characterized by a winter maximum, the highest levels and interseasonal difference being observed at the Portuguese coastal site of AVE. Surprisingly, at this site, the contribution of resin acids to the identifiable organic compounds may exceed 80% during wintry weather conditions (Figure 5). At the other locations, these wood smoke tracers represent a fraction of the identifiable organic matter ranging from about 20% to 40%, showing that domestic biomass burning is the greatest contributor to the organic matter. Dehydroabietic acid has been proposed as a candidate marker compound for coniferous wood combustion [*Standley and Simoneit*, 1994; *Rogge et al.*, 1998]. It was the major resin acid quantified in the aerosols, presenting average concentrations between 6 ng $m^{-3}$ and 44 ng $m^{-3}$ in KPZ and AVE, respectively, the two sites with the highest abundance. The other locations revealed average concentrations between 0.03 ng $m^{-3}$ and 0.61 ng $m^{-3}$. Dehydroabietic acid was not identified in aerosols from Nigeria and Amazonia, in accordance with the absence of conifer vegetation in those regions [*Simoneit et al.*, 1988, 1990]. In cities where wood is used for heating, ambient dehydroabietic acid concentrations ranged from 48 to 440 ng $m^{-3}$ [*Standley and Simoneit*, 1994]. The compound was also detected in oceanic samples at concentrations ranging from 0.0001 to 0.4 ng $m^{-3}$, whereas in terrestrial aerosol particulate matter, it was present at much higher levels (0.23–440 ng $m^{-3}$). The presence of this tracer in atmospheric matter over the ocean confirmed the long-range transport of smoke from biomass burning of the continents [*Simoneit and Elias*, 2000; *Simoneit et al.*, 2004].

### 3.3. Lipid Source Assignment

[28] The apportionment of various lipids to sources is provided in Figure 6, taking into consideration different contributions: plant waxes, microbial components, petroleum residues with other thermally matured components and pyrogenic constituents [*Simoneit et al.*, 1988; *Pio et al.*, 2001b]:

[29] 1. The contribution of plant wax includes the summation of the wax $C_n$ concentrations for *n*-alkanes; *n*-alkanoic acids, $C_{22}$–$C_{34}$; *n*-alkanols, $C_{22}$–$C_{34}$; *n*-alkan-2-ones, $C_{22}$–$C_{35}$; *n*-alkanals, $C_{22}$–$C_{35}$; and biogenic molecular markers, such as phytosterols.

[30] 2. The contribution of microbial components includes the summation of the concentrations of *n*-alkanoic acids, $C_{10}$–$C_{18}$ with CPI > 2; *n*-alkan-2-ones, $C_{15}$–$C_{21}$; and *n*-alkanols, $C_{12}$–$C_{20}$.

[31] 3. The contribution of petroleum residues includes the summation of the concentrations of anthropogenic *n*-alkanes (Total $C_n$ − Wax $C_n$) and the corresponding unresolved complex mixture; *n*-alkanoic acids, $C_{10}$–$C_{18}$, with CPI < 1.5; alkylcyclohexanes; alkylcylopentanes; hopanes; steranes; diasteranes; pristane; phytane; ketones and aldehydes with CPI < 1.5.

[32] 4. The contribution of pyrogenic compounds includes the summation of the concentrations of PAH (anthracene, phenanthrene and all the PAH with molecular ions at *m*/*z* 202, 228, 252, 278 and 300).

[33] Quasi-absent at AZO, the seasonal cycle of wax components is characterized by a summer maximum at the other sites, the highest level being observed at the black forest site of SIL. Excepting for SBO, the thermally

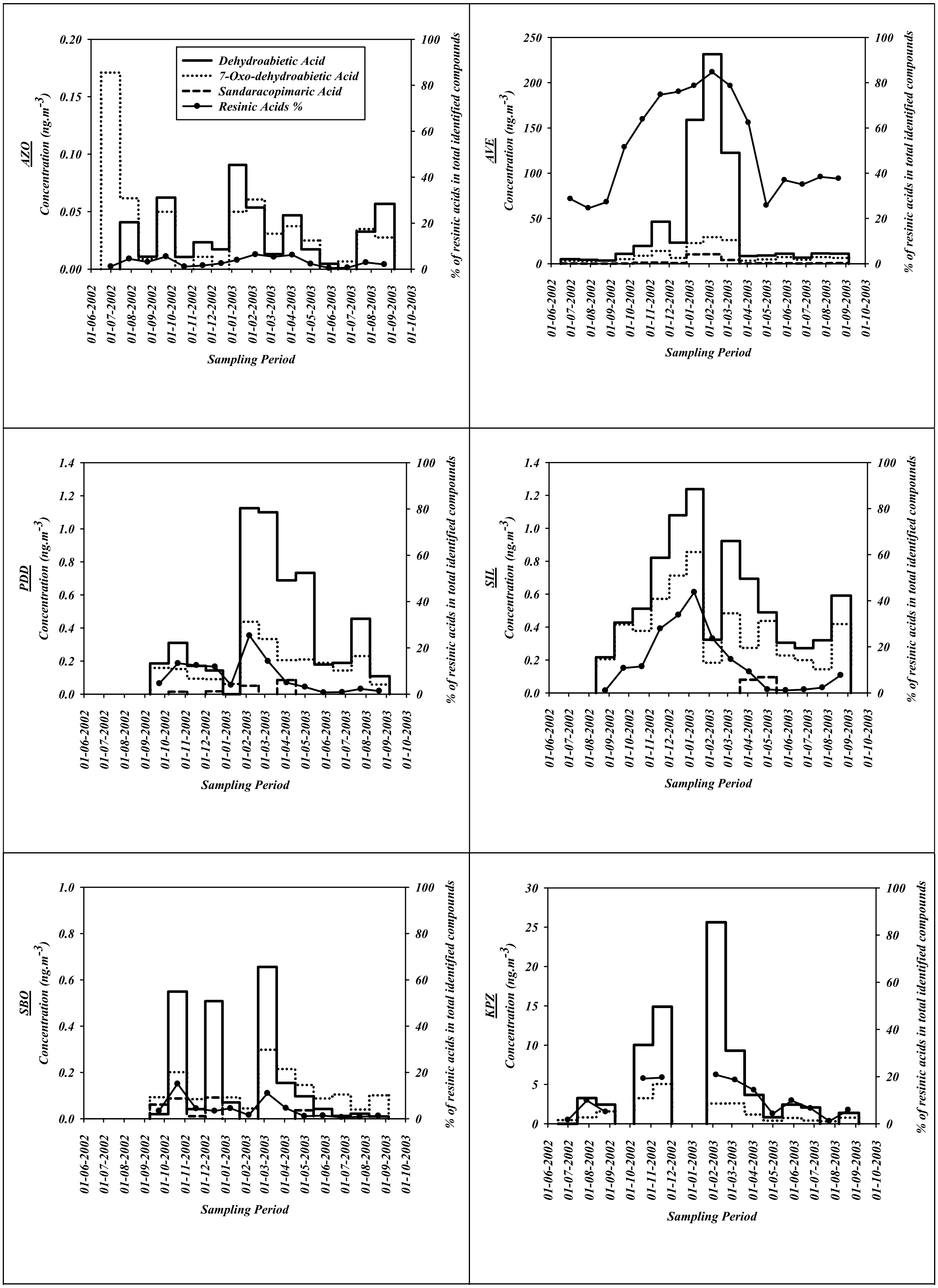
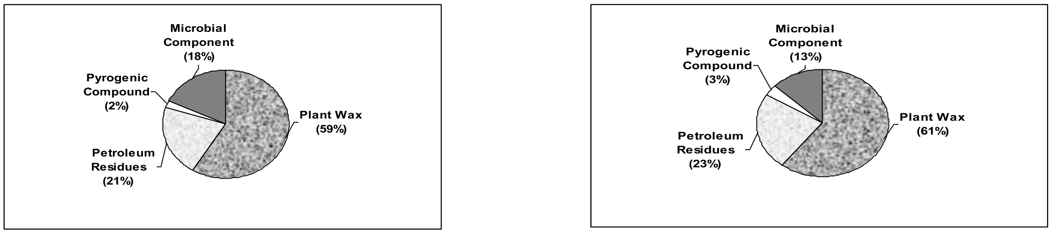
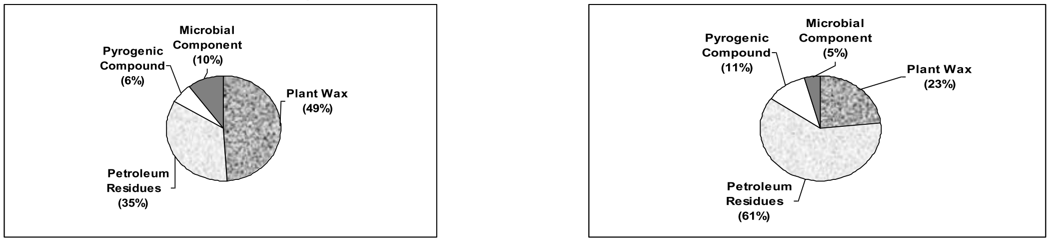


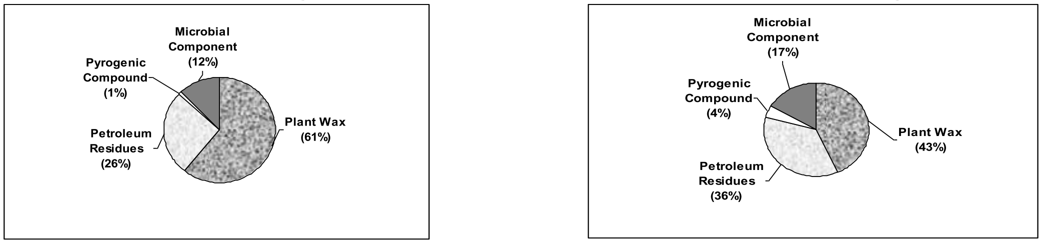
**Figure 5.** Monthly average concentration of some resin acids and their contribution to the identifiable organic matter illustrating the significant input of wood smoke constituents in wintertime, particularly at the low-level sites.



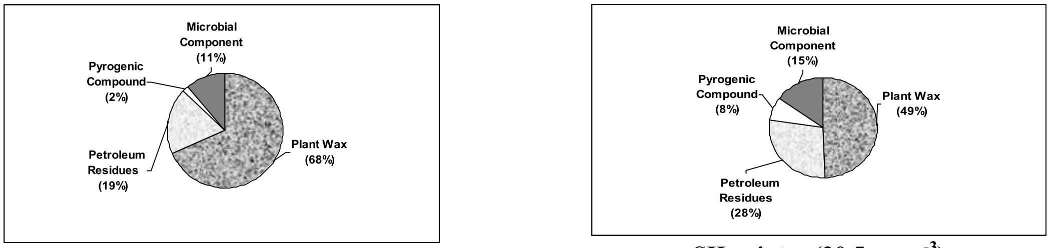
**AZO summer (15.3 ng m$^{-3}$)** **AZO winter (8.3 ng m$^{-3}$)**



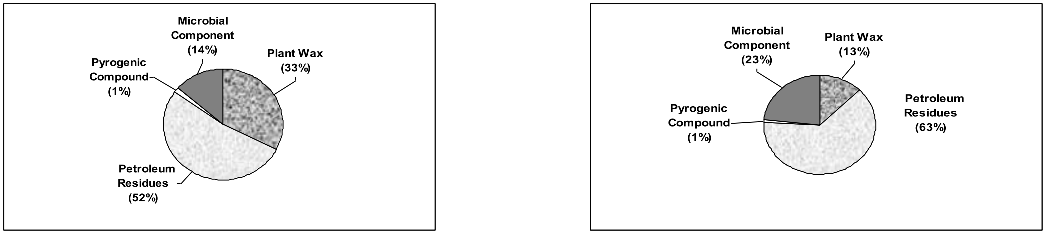
**AVE summer (99.1 ng m$^{-3}$)** **AVE winter (237.4 ng m$^{-3}$)**



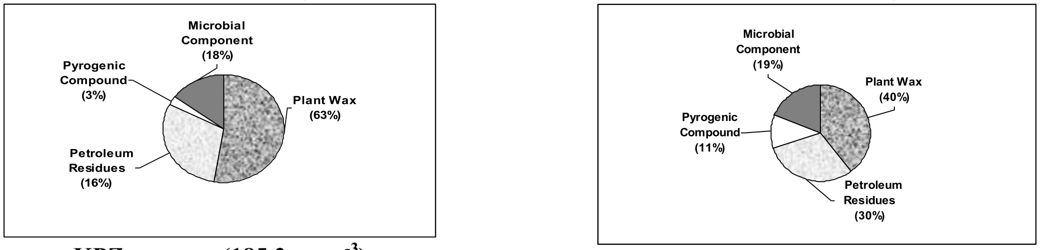
**PDD summer (61.0 ng m$^{-3}$)** **PDD winter (14.6 ng m$^{-3}$)**



**SIL summer (71.8 ng m$^{-3}$)** **SIL winter (20.5 ng m$^{-3}$)**



**SBO summer (45.4 ng m$^{-3}$)** **SBO winter (27.0 ng m$^{-3}$)**



**KPZ summer (185.3 ng m$^{-3}$)** **KPZ winter (293.1 ng m$^{-3}$)**

**Figure 6.** Pie diagrams comparing the seasonal source assignment of solvent-extractable and chromatographically resolved organic compounds in particulate matter collected in CARBOSOL sites from July 2002 to September 2003 reflecting the importance of vegetation biomass to the “waxy” portion of aerosols.

matured components represented the second more significant fraction, contributing up to 63% of the apportioned mass. It is possible that construction at SBO during the CARBOSOL project have led to contamination of the aerosol samples. Both petrogenic and pyrogenic constituents present a clear seasonal pattern, maximizing during winter. Besides the contribution of fossil fuel combustion, during wintry weather conditions, biomass burning primary emissions represent an additional anthropogenic source. The aerosol microbial component presents higher percentages during summer for the Portuguese sites (AZO and AVE), whereas a reverse seasonal trend is observed on the other locations. The contribution of petroleum residues and other thermally produced constituents at the nonurban European sites is comparable to those reported for rural Nigeria (41%) [*Simoneit et al.*, 1988], Amazonia (19%) [*Simoneit et al.*, 1990], and a forest in Greece (26%) [*Alves*, 2001]. The fractions of microbial components are of the same order than those of the Nigerian and Greek aerosols (13–16%), but lower than the one half of the apportioned organic mass in the Amazon particulate matter.

### 3.4. Organic Carbon Apportionment

[34] The source contributions of different emission sources to solvent-extractable and chromatographically identifiable organic compounds in aerosols calculated by grouping different species into different sources could have large uncertainty and be biased, because a specific compound could have two or more sources. In addition, it should be remembered that the apportioned chromatographically identifiable organic compounds represent a small fraction of total OC. Organic molecular markers have been used in conjunction with the chemical mass balance (CMB) model to apportion ambient OC to biomass smoke and other primary sources [e.g., *Robinson et al.*, 2006, and references therein]. The source profiles for receptor model application are relatively well established for urban environments, but fail in what respects natural emissions in background sites. Using these models to apportion ambient OC to different source classes relies on some challenging assumptions: (1) compositions of source emissions are constant over the period of ambient and source sampling, (2) chemical species do not react with each other, and (3) all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized. Once again, these assumptions are somewhat well met in most urban environments where source emissions remain quite constant. In this study, instead of running the CMB model, marker-to-OC mass ratios were used to roughly estimate the contribution of the most important emissions to primary organic aerosol. Calculations were focused on chemical tracers for biomass burning, cooking and motor vehicle emissions, which together were estimated to contribute to more than 90% of the ambient OC in almost all sites.

[35] Cholesterol has been used to estimate the contribution of food cooking to primary organic aerosol. Although it is thought to be a good marker for cooking, a recent investigation has reported high emissions of cholesterol resulting from prescribed burns [*Lee et al.*, 2005]. Given that wood can be used for cooking, some overlap between the two types of emission profiles may occur. The cholesterol/OC ratio of 375 pg/$\mu$g was obtained from the SPECIATE 4.0 database developed by the United States Environmental Protection Agency. A composite speciation profile for cooking was chosen as an indication of the central tendency for this source category. Calculations based on this ratio demonstrate that the contribution of emissions from cooking operations did not present a clear pattern of seasonal variation, comprising up to 30% of the primary organic carbon. The highest contribution was observed at the remote marine site, whereas a minimum value of 9% was obtained at AVE. However, if the apportionment of OC with the same key marker is based on the *Schauer et al.* [1999a] food cooking profiles, then the contribution of this emissions to OC are estimated to be 40% smaller. These results exemplify the variability of source profiles and the biases associated with the utilization of different marker-to-OC ratios depending on food type and cooking technique.

[36] The most commonly used markers for emissions from gasoline- and diesel-powered motor vehicles are isoprenoids and tricyclic terpanes. Nevertheless, these fossil-fuel-related constituents were absent in almost all the samples, excepting at AVE. In alternative, an UCM/OC average ratio of 0.783 mg/mg was used to estimate the amount of ambient organic carbon apportioned to vehicle exhausts [*Schauer et al.*, 1999b, 2002]. At the European nonurban sites, this source was estimated to contribute up to 2.6% of the ambient OC, showing a slightly higher contribution in winter compared with summer.

[37] On the basis of an average OC/dehydroabietic acid ratio of 137 $\mu$g/$\mu$g obtained by *Fine et al.* [2004] for fine particle emissions from the wood stove combustion of prevalent United States tree species, a rough estimate of the contribution of wood burning to the total amount of OC was performed. Particularly at the lowland sites, it was found that in wintertime the major fraction of OC was chiefly related to biomass combustion. At AVE, this contribution was estimated to represent always more than 85% during the cold season, decreasing to 20–55% in the summer months. In spite of a less pronounced contribution at the marine and mountain locations, this source still represents a significant input to OC. The ratios proposed in the literature for deriving the amount of OC from wood or biomass combustion in ambient aerosols vary substantially for different burning conditions and wood categories [*Robinson et al.*, 2006]. Marker-to-OC ratios appropriate for European biofuels and combustor types have yet to be determined; consequently, while the estimate presented here suggests that wood burning may be the dominant wintertime source of OC at these sites, specific source characterization are needed to confirm this finding.

## 4. Conclusions

[38] Documenting temporal and spatial variation in organic aerosol characteristics is required for both process studies and to support modeling efforts. In this study, an extensive data set for nonurban sites in western/central Europe was gathered showing that the carbonaceous content in the aerosol from the Azorean archipelago was 2 to 20 times lower than the results obtained for continental areas. An absence of seasonal variation was observed for

this oceanic site. The highest OC and EC concentrations were recorded at lowland rural continental areas (Aveiro and K-puszta), where a threefold to fivefold enrichment of carbonaceous material was registered, when compared with the high-altitude sites (Puy de Dôme, Schauinsland and Sonnblick). The quantification of organic compounds in atmospheric samples indicated that biomass burning, vegetation, fossil fuel consumption and meat cooking represented the main sources of identifiable organic aerosol components. In accordance with a close proximity to an urban area, petroleum markers were detected mainly in Aveiro. The continental low-level sites registered the highest levels of lipophilic organic compounds, with winter maxima dominating the seasonal variation. The increase in the winter levels is due to a sizable contribution of wood burning and meat cooking operations, as demonstrated by an increase in the amounts of specific molecular markers (e.g., resin acids and cholesterol). Different modal distributions of both homologous series of straight chain compounds and phytosterols, suggest that the steroid and vegetation wax patterns may be related to geographical characteristics, particularly, the specific plant communities and the climatic conditions. Relative contributions of plant waxes to organic matter increase with elevation and since these constituents are believed rather long-lived with respect to atmospheric oxidation processes, they may be enriched on the route to background regions. In general, ratios between saturated and unsaturated fatty acids presented higher values during the cold season at all locations, suggesting that there were more aged aerosols in winter, while more fresh emissions were found in summer. In spite of the geographical heterogeneity in the presented data set, we consider that it encloses relevant information which cannot be obtained from routine aerosol monitoring. Concentrations of some organic species in some background sites can be high as levels at nonrural locations in other parts of Europe, which show the importance of regional and long-range transport processes of emissions, in addition to local sources.

[39] While fossil fuel related sources predominate throughout the year at all sites, domestic wood burning presents a remarkably high share in the wintry European aerosol background, a finding that has not been presented earlier. In fact, it was estimated that biomass combustion may represent more than 80% of the particulate organic carbon in the rural atmosphere. Though it is substantially less important in summer, because of forest and agricultural fires, this source still contributes significantly more to OC than fossil fuel primary emission. In Europe, data on detailed emission factors from biomass burning are scarce. Emission inventories, source apportionment, photochemistry and climate change models use default values obtained for US biofuels, uncommon in Europe. Thus it is desirable to use more specific locally available data. Taking into account that the present study has established biomass burning as the greatest contributor to OC in Europe and that wood smoke components are nonnegligible even at elevated background sites, it stresses the necessity of obtaining detailed source emission profiles for distinct biofuels and types of biomass combustion.

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